

WEST

 Generate Collection

L12: Entry 5 of 25

File: USPT

Oct 23, 2001

US-PAT-NO: 6306808

DOCUMENT-IDENTIFIER: US 6306808 B1

** See image for Certificate of Correction **

TITLE: Manganese complexes as catalysts for peroxygenated compounds to clean hard surfaces, especially dishes

DATE-ISSUED: October 23, 2001

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|-------------|-------|----------|---------|
| Hazenkamp; Menno | Basel | | | CH |
| Dubs; Marie-Josee | Wittersdorf | | | FR |
| Bachmann; Frank | Freiburg | | | DE |
| Schlingloff; Gunther | Riehen | | | CH |
| Allemann; Rachel | Saint-Louis | | | FR |
| Dannacher; Josef | Basel | | | CH |

ASSIGNEE-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY | TYPE CODE |
|--------------------------------------|-----------|-------|----------|---------|-----------|
| Ciba Specialty Chemicals Corporation | Tarrytown | NY | | | 02 |

APPL-NO: 09/ 763017 [PALM]

DATE FILED: February 15, 2001

FOREIGN-APPL-PRIORITY-DATA:

| COUNTRY | APPL-NO | APPL-DATE |
|---------|----------|-----------------|
| EP | 98810811 | August 19, 1998 |

PCT-DATA:

| APPL-NO | DATE-FILED | PUB-NO | PUB-DATE | 371-DATE | 102 (E) -DATE |
|----------------|----------------|------------|-------------|--------------|---------------|
| PCT/EP99/05699 | August 6, 1999 | WO00/11129 | Feb 3, 2000 | Feb 15, 2001 | Feb 15, 2001 |

INT-CL: [07] C11 D 7/38, C11 D 7/54

US-CL-ISSUED: 510/224; 510/221, 510/372, 510/376, 510/378, 252/186.29, 252/186.33, 134/25.2

US-CL-CURRENT: 510/224; 134/25.2, 252/186.29, 252/186.33, 510/221, 510/372, 510/376, 510/378

FIELD-OF-SEARCH: 510/220, 510/221, 510/224, 510/372, 510/376, 510/378, 252/186.29, 252/186.33, 134/25.2

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

| PAT-NO | ISSUE-DATE | PATENTEE-NAME | US-CL |
|---|--------------|-----------------|---------|
| <input type="checkbox"/> <u>5733341</u> | March 1998 | Eckhardt et al. | 8/111 |
| <input type="checkbox"/> <u>5741920</u> | April 1998 | Eckhardt et al. | 556/45 |
| <input type="checkbox"/> <u>5965506</u> | October 1999 | Bacher et al. | 510/311 |
| <input type="checkbox"/> <u>6228127</u> | May 2001 | Reinehr et al. | 8/111 |

FOREIGN PATENT DOCUMENTS

| FOREIGN-PAT-NO | PUBN-DATE | COUNTRY | US-CL |
|----------------|---------------|---------|-------|
| 630964 | December 1994 | EP | |
| 693550 | January 1996 | EP | |
| 902083 | March 1999 | EP | |
| 2306472 | May 1997 | GB | |
| WO 97/07191 | February 1997 | WO | |

ART-UNIT: 171

PRIMARY-EXAMINER: Delcotto; Gregory

ATTY-AGENT-FIRM: Mansfield; Kevin T.

ABSTRACT:

The present invention relates to the use of certain manganese complexes as catalysts for reactions with peroxy compounds for bleaching colored stains on hard surfaces. The invention also relates to cleaning agents for hard surfaces comprising such manganese catalysts.

10 Claims, 0 Drawing figures

WEST

 Generate Collection

L12: Entry 5 of 25

File: USPT

Oct 23, 2001

US-PAT-NO: 6306808

DOCUMENT-IDENTIFIER: US 6306808 B1

**** See image for Certificate of Correction ****

TITLE: Manganese complexes as catalysts for peroxygenated compounds to clean hard surfaces, especially dishes

DATE-ISSUED: October 23, 2001

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|-------------|-------|----------|---------|
| Hazenkamp; Menno | Basel | | | CH |
| Dubs; Marie-Josee | Wittersdorf | | | FR |
| Bachmann; Frank | Freiburg | | | DE |
| Schlingloff; Gunther | Riehen | | | CH |
| Allemann; Rachel | Saint-Louis | | | FR |
| Dannacher; Josef | Basel | | | CH |

US-CL-CURRENT: 510/224; 134/25.2, 252/186.29, 252/186.33, 510/221, 510/372, 510/376,
510/378

CLAIMS:

What is claimed is:

1. A method of cleaning a hard surface, which comprises contacting the surface with a solution containing a peroxy compound and, as catalyst for the peroxy compound, a manganese complex of the formula (1) or (2) ##STR8##

wherein

Y is linear or branched alkylene of formula --[C(R._{sub.1}).sub.2].sub.m, wherein m is an integer from 2 to 8 and each R._{sub.1} is independently hydrogen or C._{sub.1}-C._{sub.4} alkyl; --CX.dbd.CX--, wherein X is cyano, linear or branched C._{sub.1}-C._{sub.8} alkyl or di(linear or branched C._{sub.1}-C._{sub.8} alkyl)amino; --(CH._{sub.2}).sub.q --NR._{sub.1}--(CH._{sub.2}).sub.q --, wherein R._{sub.1} is as defined and q is 1, 2, 3 or 4; or a 1,2-cyclohexylene or 1,2-phenylene radical of formula ##STR9##

wherein R._{sub.8} is hydrogen, CH._{sub.2} OH, CH._{sub.2} NH._{sub.2} or SO._{sub.3} M, wherein M is hydrogen; an alkali metal atom, ammonium or the cation of an organic amine,

R._{sub.5} and R._{sub.6} are each independently of the other hydrogen; linear or branched C._{sub.1}-C._{sub.4} alkyl; linear or branched C._{sub.1}-C._{sub.8} alkylene-R._{sub.2}, wherein R._{sub.2} is OR._{sub.1}, COOR._{sub.1} or NR._{sub.3} R._{sub.4}; unsubstituted aryl or aryl substituted by cyano, halogen, OR._{sub.1}, COOR._{sub.1}, nitro, linear or branched C._{sub.1}-C._{sub.8} alkyl, NR._{sub.3} R._{sub.4}, wherein R._{sub.3} and R._{sub.4} are each independently of the other hydrogen or linear or branched C._{sub.1}-C._{sub.12} alkyl, or by --N.sup..sym. R._{sub.1} R._{sub.3} R._{sub.4}, wherein R._{sub.1}, R._{sub.3} and R._{sub.4} are as previously defined,

each R._{sub.7} independently of the others is hydrogen or C._{sub.1}-C._{sub.4} alkyl,

Z.sub.1 and Z.sub.2 are each independently of the other hydrogen, hydroxy, C.sub.1 -C.sub.4 alkoxy or di(C.sub.1 -C.sub.4 alkyl)amino, and

A is a charge-balancing anionic ligand, with the proviso that, in the compounds of the formula (1), when Y is 1,2-phenylene the substituents Z.sub.1, Z.sub.2, R.sub.5 and R.sub.6 may not all simultaneously be hydrogen.

2. A method of cleaning a hard surface, wherein the hard surface comprises table- or kitchen-ware.

3. A method according to claim 1 wherein, in formula (1), Z.sub.1 and Z.sub.2 are each independently of the other hydrogen, hydroxy, methoxy, ethoxy, dimethylamino or diethylamino.

4. A method according to claim 1 wherein, in formula (1) and (2), Y is ethylene, 1,2- or 1,3-propylene, 1-methyl-1,2-propylene, 2-methyl-1,2-propylene, 1,2-cyclohexylene or 1,2-phenylene.

5. A method according to claim 4, wherein Y is ethylene, 1,3-propylene, 2-methyl-1,2-propylene, 1,2-cyclohexylene or 1,2-phenylene.

6. A method according to claim 1 wherein, in formula (1) and (2), R.sub.5 and R.sub.6 are each independently of the other hydrogen, methyl, ethyl or unsubstituted phenyl.

7. A method according to claim 1 wherein, in formula (2), each R.sub.7 independently of the others is hydrogen, methyl or ethyl.

8. A method according to claim 1, wherein the charge-balancing anionic ligand A in the compound of formula (1) or (2) is halide, hydroxide, hexafluorophosphate, perchlorate or the anion of an organic carboxylic acid.

9. A method according to claim 1, wherein the peroxy compound is selected from the group consisting of organic peracids, hydrogen peroxide, perborate and percarbonate, and mixtures thereof.

10. A method according to claim 1, wherein there is additionally used a bleach activator.

WEST

 Generate Collection

L12: Entry 5 of 25

File: USPT

Oct 23, 2001

DOCUMENT-IDENTIFIER: US 6306808 B1

** See image for Certificate of Correction **

TITLE: Manganese complexes as catalysts for peroxygenated compounds to clean hard surfaces, especially dishes

Brief Summary Text (2):

Inorganic peroxy compounds, especially hydrogen peroxide and solid peroxy compounds that dissolve in water with the release of hydrogen peroxide, such as sodium perborate and sodium carbonate perhydrate, have long been used as oxidising agents for disinfection and bleaching purposes. The oxidising action of such substances in dilute solutions is highly dependent upon temperature. For example, using H.sub.2 O.sub.2 or perborate in alkaline bleaching liquors it is only at temperatures above about 80.degree. C. that sufficiently rapid bleaching of soiled textiles is achieved. At lower temperatures, the oxidising action of the inorganic peroxy compounds can be improved by the addition of so-called bleach activators, for which numerous proposals have been disclosed in the literature. They are especially compounds from the substance classes of the N- and O-acyl compounds, for example polyacylated alkylendiamines, especially tetraacetylthylenediamine, acylated glycolurils, especially tetraacetylglycoluril, N-acylated hydantoins, hydrazides, triazoles, hydrotriazines, urazoles, diketopiperazines, sulfurylamides and cyanurates, and in addition carboxylic acid anhydrides, especially phthalic anhydride, carboxylic acid esters, especially sodium nonanoyloxybenzenesulfonate, sodium isonanoyloxybenzenesulfonate, and acylated sugar derivatives, such as pentaacetylglucose. By the addition of such substances, the bleaching action of aqueous peroxide liquors can be increased to such an extent that even at temperatures of around 60.degree. C. their action is substantially the same as that of the peroxide liquor alone at 95.degree. C.

Brief Summary Text (34):

There come into consideration, for example, polyacrylic acids and copolymers of maleic anhydride and acrylic acid and also the sodium salts of those polymeric acids. Commercially available products are, for example, Sokalan.RTM. CP 5 and PA 30 from BASF. Polymers of natural origin that can be used as co-builders include, for example, oxidised starch, as known, for example, from International Patent Application WO 94/05762, and polyamino acids, such as polyglutamic acid or polyaspartic acid. Further possible builder components are naturally occurring hydroxycarboxylic acids, e.g. mono- and di-hydroxysuccinic acid, alpha.-hydroxypropionic acid and gluconic acid. There also come into consideration as builder components the salts of citric acid, especially sodium citrate. As sodium citrate there come into consideration anhydrous trisodium citrate and especially trisodium citrate dihydrate. Trisodium citrate dihydrate can be used in the form of a fine- or coarse-crystalline powder. Depending upon the pH value ultimately established in the agents according to the invention, the acids corresponding to the mentioned co-builder salts may also be present.

Brief Summary Text (35):

Oxygen-based bleaching agents that come into consideration include especially alkali metal perborate mono- and tetra-hydrate and/or alkali metal percarbonate, sodium being the preferred alkali metal. The use of sodium percarbonate has advantages especially in cleaning agents for table- and kitchen-ware, since it has a particularly advantageous effect on corrosion behaviour in glasses. In addition, or especially alternatively, it is also possible for known peroxy-carboxylic acids to be present, for example dodecane-diperacid or phthalamidopercarboxylic acids, which may

be unsubstituted or substituted on the aromatic moiety. Furthermore, the addition of small amounts of known bleaching agent stabilisers, for example phosphonates, borates or metaborates and metasilicates, and also magnesium salts, such as magnesium sulfate, may be advantageous.

Brief Summary Text (36) :

In addition to the bleach catalysts according to formula (1) or (2) it is also possible to use further known transition metal salts or complexes known as bleach-activating active ingredients and/or conventional bleach activators, that is to say compounds that, under perhydrolysis conditions, yield unsubstituted or substituted perbenzo- and/or peroxy-carboxylic acids having from 1 to 10 carbon atoms, especially from 2 to 4 carbon atoms. Suitable bleach activators include the customary bleach activators, mentioned at the beginning, that carry O- and/or N-acyl groups having the indicated number of carbon atoms and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetyl ethylenediamine (TAED), acylated glycolurils, especially tetraacetyl glycoluril (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated phenylsulfonates, especially nonanoyloxy- or isononanoyloxy-benzenesulfonate, acylated polyvalent alcohols, especially triacetin, ethylene glycol diacetate and 2,5-di-acetoxy-2,5-dihydrofuran, and also acetylated sorbitol and mannitol and acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), penta-acetylfructose, tetraacetylxylose and octaacetyl lactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. It is also possible to use the combinations of conventional bleach activators known from German Patent Application DE-A-44 43 177.

Detailed Description Text (9) :

The cups are cleaned in a Miele G-690 D dishwasher on the delicate programme at 45.degree. C. using hard water. In each cleaning programme 12 tea-stained cups are cleaned. The machine also contains six glasses with milk stains, 24 clean plates and 60 g of a mixture of different foodstuffs (inter alia spinach, egg, minced meat, starch). The dose of dishwashing agent is: 17.2 g of a phosphate-containing base formulation, 1.72 g of sodium perborate monohydrate, 0.8 g of TAED and, as appropriate, 50 ppm of catalyst (ppm based on the metal). After the cleaning operation, the removal of the tea deposit is evaluated visually on a scale from 0 (=unchanged, very strong deposit) to 10 (=no deposit). Table 1 shows the ratings for our catalysts compared with a reference (TAED only, no catalyst). The ratings indicated in the Table are the median values from several cleaning programmes each using 12 cups. The Table shows that the ratings for the catalysts used according to the invention are significantly better than the reference value.

Detailed Description Text (10) :

Similar results are obtained when a dishwashing agent of the following composition is used together with 50 ppm of the catalysts used in the above Table, 1.72 g of sodium perborate monohydrate and 0.8 g of TAED.

Detailed Description Text (12) :

10.1 mg (30 .mu.mol) of morin dihydrate are dissolved in 1000 ml of a borax buffer solution (9 mmol of disodium tetraborate/liter, pH=9.4). At t=0 min., 295 mg (2.5 mmol) of sodium perborate monohydrate and, as appropriate, 3.4 .mu.mol of catalyst or 137 mg (0.6 mmol) of TAED are added. Over a period of 30 minutes, the extinction E of the solution at 400 nm is measured at 27.degree. C. at one minute intervals. The values for the percentage decoloration D(t), calculated in accordance with $D(t) = [E(0) - E(t)] / E(0) * 100$, are indicated in Table 2.

CLAIMS:

9. A method according to claim 1, wherein the peroxy compound is selected from the group consisting of organic peracids, hydrogen peroxide, perborate and percarbonate, and mixtures thereof.